US009200192B2

(12) **United States Patent**
Zelenev et al.

(10) **Patent No.: US 9,200,192 B2**

(45) **Date of Patent: Dec. 1, 2015**

(54) **COMPOSITIONS AND METHODS FOR ENHANCEMENT OF PRODUCTION OF LIQUID AND GASEOUS HYDROCARBONS**

(71) Applicant: **CESI Chemical, Inc.**, Houston, TX (US)

(72) Inventors: **Andrei Zelenev**, Spring, TX (US); **Lakia M. Champagne**, The Woodlands, TX (US); **Bill Zhou**, The Woodlands, TX (US); **Nathan L. Lett**, Cypress, TX (US); **Keith Ingram Dismuke**, Katy, TX (US); **Glenn S. Penny**, Lakewood, CO (US)

(73) Assignee: **CESI Chemical, Inc.**, Houston, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 303 days.

(21) Appl. No.: **13/889,709**

(22) Filed: **May 8, 2013**

(65) **Prior Publication Data**

US 2014/0299325 A1 Oct. 9, 2014

Related U.S. Application Data

(60) Provisional application No. 61/644,419, filed on May 8, 2012.

(51) **Int. Cl.**

E21B 43/16	(2006.01)
C09K 8/60	(2006.01)
E21B 43/30	(2006.01)
C09K 8/584	(2006.01)

(52) **U.S. Cl.**

CPC ***C09K 8/602*** (2013.01); ***C09K 8/584*** (2013.01); ***E21B 43/30*** (2013.01)

(58) **Field of Classification Search**

CPC E21B 43/12; E21B 43/16; E21B 43/25

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,060,210	A	4/1961	De Groote
3,047,062	A	7/1962	Meadors
3,347,789	A	10/1967	Dickson et al.
3,368,624	A	2/1968	Heuer et al.
3,483,923	A	12/1969	Darley
3,710,865	A	1/1973	Kiel
3,756,319	A	9/1973	Holm et al.
3,760,881	A	9/1973	Kiel
3,850,248	A	11/1974	Carney
3,919,411	A	11/1975	Glass et al.
4,005,020	A	1/1977	McCormick
4,206,809	A	6/1980	Jones
4,233,165	A	11/1980	Salathiel et al.
4,276,935	A	7/1981	Hessert et al.
4,360,061	A	11/1982	Canter et al.
4,414,128	A	11/1983	Goffinet
4,472,291	A	9/1984	Rosano
4,511,488	A	4/1985	Matta
4,650,000	A	3/1987	Andreasson et al.
4,844,756	A	7/1989	Forsberg
5,008,026	A	4/1991	Gardner et al.
5,034,140	A	7/1991	Gardner et al.
5,076,954	A	12/1991	Loth et al.
5,083,613	A	1/1992	Gregoli et al.
5,095,989	A	3/1992	Prukop
5,217,531	A	6/1993	Cheung
5,247,995	A	9/1993	Tjon-Joe-Pin et al.
5,310,002	A	5/1994	Blauch et al.
5,356,482	A	10/1994	Mehta et al.
5,567,675	A	10/1996	Romocki
5,587,354	A	12/1996	Duncan, Jr.
5,587,357	A	12/1996	Rhinesmith
5,604,195	A	2/1997	Misselyn et al.
5,652,200	A	7/1997	Davies et al.
5,665,689	A	9/1997	Durbut
5,676,763	A	10/1997	Salisbury et al.
5,697,458	A	12/1997	Carney
5,707,940	A	1/1998	Bush et al.
5,762,138	A	6/1998	Ford et al.

(Continued)

FOREIGN PATENT DOCUMENTS

CN	102127414	7/2011
CN	102277143	12/2011

(Continued)

OTHER PUBLICATIONS

International Search Report and Written Opinion dated Oct. 21, 2014 for Application No. PCT/US2014/37334.

[No Author Listed], The HLB system: a time-saving guide to emulsifier selection. ICI Americas Inc. 1976. 22 pages.

ADM, Evolution Chemicals E5789-117 Description. Jun. 2014.

Brost et al., Surfactants assist water-in-oil monitoring by fluroescence. World Oil. Oct. 2008;229(10).

Champagne et al., Critical assessment of microemulsion technology for enhancing fluid recovery from tight gas formations and propped fractures. SPE European Formation Damage Conference. Noordwijk, The Netherlands. Jun. 7-10, 2011. SPE-144095. 10 pages.

Crafton et al., Micro-emulsion effectiveness for twenty four wells, eastern green river, wyoming. 2009 SPE Rocky Mountain Petroleum Technology Conference. Denver, Colorado, USA, Apr. 14-16, 2009. SPE-123280. 13 pages.

Haw, The HLB system: a time saving guide to surfactant selection. Presentation to the Midwest chapter of the society of cosmetic chemists. Uniqema. Mar. 9, 2004. 39 slides.

(Continued)

Primary Examiner — Catherine Loikith

(74) *Attorney, Agent, or Firm* — Wolf, Greenfield & Sacks, P.C.

(57) **ABSTRACT**

A well treatment composition is well-designed for the simultaneous enhancement of the production of both liquid and gaseous hydrocarbons from the same reservoir on a non-selective basis. The well treatment composition includes a first surfactant and a second surfactant, wherein the second surfactant is selected from the group consisting of ethoxylated alkylene amines, ethoxylated alkyl amines, propoxylated alkylene amines, propoxylated alkyl amines, ethoxylated-propoxylated alkylene amines and ethoxylated-propoxylated alkyl amines. The well treatment composition also includes a first solvent, a second solvent and water. Methods for using the well treatment composition include the steps of emplacing the well treatment composition into wells having high and low gas-to-oil ratios.

18 Claims, No Drawings

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,784,386 A 7/1998 Norris
5,811,383 A 9/1998 Klier et al.
5,830,831 A 11/1998 Chan et al.
5,874,386 A 2/1999 Chan et al.
5,925,233 A 7/1999 Miller et al.
5,975,206 A 11/1999 Woo et al.
5,977,032 A 11/1999 Chan
5,990,072 A 11/1999 Gross et al.
5,996,692 A 12/1999 Chan et al.
6,046,140 A 4/2000 Woo et al.
6,090,754 A 7/2000 Chan et al.
6,110,885 A 8/2000 Chan
6,112,814 A 9/2000 Chan et al.
6,165,946 A 12/2000 Mueller et al.
6,173,776 B1 1/2001 Furman et al.
6,191,090 B1 2/2001 Mondin et al.
6,228,830 B1 5/2001 Vlasblom
6,260,621 B1 7/2001 Furman et al.
6,302,209 B1 10/2001 Thompson, Sr. et al.
6,364,020 B1 4/2002 Crawshaw et al.
6,486,115 B1 11/2002 Weaver et al.
6,581,687 B2 6/2003 Collins et al.
6,593,279 B2 7/2003 Von Krosigk et al.
6,613,720 B1 9/2003 Feraud et al.
6,729,402 B2 5/2004 Chang et al.
6,770,603 B1 8/2004 Sawdon et al.
6,793,025 B2 9/2004 Patel et al.
6,800,593 B2 10/2004 Dobson, Jr. et al.
6,818,595 B2 11/2004 Benton et al.
6,911,417 B2 6/2005 Chan et al.
6,914,040 B2 7/2005 Deak et al.
6,939,832 B2 9/2005 Collins
6,984,610 B2 1/2006 VonKrosigk et al.
7,021,378 B2 4/2006 Prukop
7,134,496 B2 11/2006 Jones et al.
7,205,262 B2 4/2007 Schwartz et al.
7,205,264 B2 4/2007 Boles
7,231,976 B2 6/2007 Berry et al.
7,380,606 B2 6/2008 Pursley et al.
7,392,844 B2 7/2008 Berry et al.
7,407,915 B2 8/2008 Jones et al.
7,468,402 B2 12/2008 Yang et al.
7,481,273 B2 1/2009 Javora et al.
7,514,390 B2 4/2009 Chan
7,514,391 B2 4/2009 Chan
7,533,723 B2 5/2009 Hughes et al.
7,543,644 B2 6/2009 Huang et al.
7,543,646 B2 6/2009 Huang et al.
7,544,639 B2 6/2009 Pursley et al.
7,547,665 B2 6/2009 Welton et al.
7,552,771 B2 6/2009 Eoff et al.
7,559,369 B2 7/2009 Roddy et al.
7,581,594 B2 9/2009 Tang
7,615,516 B2 11/2009 Yang et al.
7,621,334 B2 11/2009 Welton et al.
7,622,436 B2 11/2009 Tuzi et al.
7,655,603 B2 2/2010 Crews
7,677,311 B2 3/2010 Abad et al.
7,687,439 B2 3/2010 Jones et al.
7,709,421 B2 5/2010 Jones et al.
7,712,534 B2 5/2010 Bryant et al.
7,727,936 B2 6/2010 Pauls et al.
7,727,937 B2 6/2010 Pauls et al.
7,730,958 B2 6/2010 Smith
7,825,073 B2 11/2010 Welton et al.
7,833,943 B2 11/2010 Van Zanten et al.
7,838,467 B2 11/2010 Jones et al.
7,846,877 B1 12/2010 Robb
7,851,414 B2 12/2010 Yang et al.
7,855,168 B2 12/2010 Fuller et al.
7,857,051 B2 12/2010 Abad et al.
7,886,824 B2 2/2011 Kakadjian et al.
7,893,010 B2 2/2011 Ali et al.
7,902,123 B2 3/2011 Harrison et al.
7,906,464 B2 3/2011 Davidson
7,910,524 B2 3/2011 Welton et al.
7,931,088 B2 4/2011 Stegemoeller et al.
7,960,314 B2 6/2011 Van Zanten et al.
7,960,315 B2 6/2011 Welton et al.
7,963,720 B2 6/2011 Hoag et al.
7,971,659 B2 7/2011 Gatlin et al.
7,976,241 B2 7/2011 Hoag et al.
7,989,404 B2 8/2011 Kakadjian et al.
7,992,656 B2 8/2011 Dusterhoft et al.
7,998,911 B1 8/2011 Berger et al.
8,043,996 B2 10/2011 Harris
8,053,396 B2 11/2011 Huff et al.
8,053,397 B2 11/2011 Huang et al.
8,057,682 B2 11/2011 Hoag et al.
8,091,644 B2 1/2012 Clark et al.
8,091,645 B2 1/2012 Quintero et al.
8,091,646 B2 1/2012 Quintero et al.
8,100,190 B2 1/2012 Weaver et al.
8,148,303 B2 4/2012 Van Zanten et al.
8,183,182 B2 5/2012 Oliveira et al.
8,206,062 B2 6/2012 Hoag et al.
8,207,096 B2 6/2012 van Zanten et al.
8,210,263 B2 7/2012 Quintero et al.
8,220,546 B2 7/2012 Kakadjian et al.
8,227,382 B2 7/2012 Dakin et al.
8,231,947 B2 7/2012 Vaidya et al.
8,235,120 B2 8/2012 Quintero et al.
8,242,059 B2 8/2012 Sawdon
8,293,687 B2 10/2012 Giffin
8,342,241 B2 1/2013 Hartshorne et al.
8,349,771 B2 1/2013 Seth et al.
8,356,667 B2 1/2013 Quintero et al.
8,357,639 B2 1/2013 Quintero et al.
8,372,789 B2 2/2013 Harris et al.
8,383,560 B2 2/2013 Pich et al.
8,403,051 B2 3/2013 Huang et al.
8,404,623 B2 3/2013 Robb et al.
8,413,721 B2 4/2013 Welton et al.
8,415,279 B2 4/2013 Quintero et al.
8,431,620 B2 4/2013 Del Gaudio et al.
8,453,741 B2 6/2013 van Zanten
8,499,832 B2 8/2013 Crews et al.
8,517,100 B2 8/2013 Ali et al.
8,517,104 B2 8/2013 Kieffer
8,524,643 B2 9/2013 Huff et al.
8,551,926 B2 10/2013 Huang et al.
8,592,350 B2 11/2013 van Zanten et al.
8,684,079 B2 4/2014 Wattenbarger et al.
8,778,850 B2 7/2014 Andrecola
8,865,632 B1 10/2014 Parnell et al.
2001/0007663 A1 7/2001 Von Corswant
2003/0022944 A1 1/2003 Gumkowski et al.
2003/0069143 A1 4/2003 Collins
2003/0166472 A1 9/2003 Pursley et al.
2003/0232095 A1 12/2003 Garti et al.
2005/0209107 A1 9/2005 Pursley et al.
2006/0014648 A1 1/2006 Milson et al.
2006/0211593 A1 9/2006 Smith et al.
2006/0258541 A1 11/2006 Crews
2007/0123445 A1 5/2007 Tuzi et al.
2007/0293404 A1 12/2007 Hutchins et al.
2007/0295368 A1 12/2007 Harrison et al.
2008/0274918 A1 11/2008 Quintero et al.
2008/0287324 A1 11/2008 Pursley et al.
2009/0078415 A1 3/2009 Fan et al.
2009/0137432 A1 5/2009 Sullivan et al.
2009/0159288 A1 6/2009 Horvath Szabo et al.
2009/0221456 A1 9/2009 Harrison et al.
2009/0260819 A1 10/2009 Kurian et al.
2009/0275488 A1 11/2009 Zamora et al.
2009/0281004 A1 11/2009 Ali et al.
2010/0022421 A1 1/2010 Gutierrez et al.
2010/0173805 A1 7/2010 Pomerleau
2010/0216670 A1 8/2010 Del Gaudio et al.
2010/0243248 A1 9/2010 Golomb et al.
2010/0252267 A1 10/2010 Harris et al.
2010/0263863 A1 10/2010 Quintero et al.
2010/0272765 A1 10/2010 Ho O et al.
2010/0307757 A1 12/2010 Blow et al.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2011/0021386	A1	1/2011	Ali et al.
2011/0136706	A1	6/2011	Carroll et al.
2011/0146983	A1	6/2011	Sawdon
2011/0190174	A1	8/2011	Weerasooriya et al.
2011/0220353	A1	9/2011	Bittner et al.
2011/0237467	A1	9/2011	Cornette et al.
2011/0253365	A1	10/2011	Crews et al.
2011/0290491	A1	12/2011	Gupta et al.
2012/0004146	A1	1/2012	Van Zanten et al.
2012/0015852	A1	1/2012	Quintero et al.
2012/0035085	A1	2/2012	Parnell et al.
2012/0071366	A1	3/2012	Falana et al.
2012/0080232	A1	4/2012	Muller et al.
2012/0129738	A1	5/2012	Gupta et al.
2012/0149626	A1	6/2012	Fluck et al.
2012/0168165	A1	7/2012	Holcomb et al.
2012/0181019	A1	7/2012	Saini et al.
2012/0193095	A1	8/2012	Varadaraj et al.
2012/0208726	A1	8/2012	Smith et al.
2012/0234548	A1	9/2012	Dyer
2012/0241155	A1	9/2012	Ali et al.
2012/0241220	A1	9/2012	Quintero et al.
2012/0255887	A1	10/2012	Holms et al.
2012/0261120	A1	10/2012	Del Gaudio et al.
2012/0285690	A1	11/2012	Weaver et al.
2012/0285694	A1	11/2012	Morvan et al.
2012/0318504	A1	12/2012	Fan et al.
2012/0318515	A1	12/2012	Cawiezel et al.
2012/0322697	A1	12/2012	Zhang
2012/0325492	A1	12/2012	Fefer et al.
2013/0029883	A1	1/2013	Dismuke et al.
2013/0048281	A1	2/2013	Van Zanten et al.
2013/0079255	A1	3/2013	Del Gaudio et al.
2013/0109597	A1	5/2013	Sarkar et al.
2013/0133886	A1	5/2013	Quintero
2013/0137611	A1	5/2013	Pierce et al.
2013/0146288	A1	6/2013	Smith et al.
2013/0146545	A1	6/2013	Pabalan et al.
2013/0153232	A1	6/2013	Bobier et al.
2013/0153234	A1	6/2013	Bobier et al.
2013/0192826	A1	8/2013	Kurian et al.
2013/0233559	A1	9/2013	van Zanten et al.
2013/0244913	A1	9/2013	Maberry et al.
2013/0261033	A1	10/2013	Nguyen
2013/0292121	A1	11/2013	Penny et al.
2014/0005079	A1	1/2014	Dahanayake et al.
2014/0110344	A1	4/2014	Hoag et al.
2014/0202700	A1	7/2014	Blair
2014/0262261	A1	9/2014	Hill et al.
2014/0262274	A1	9/2014	Dismuke et al.
2014/0262288	A1	9/2014	Penny et al.
2014/0274817	A1	9/2014	Hill et al.
2014/0274822	A1	9/2014	Dismuke et al.
2014/0284053	A1	9/2014	Germack et al.
2014/0284057	A1	9/2014	Champagne et al.
2014/0332212	A1	11/2014	Ayers et al.
2014/0338911	A1	11/2014	Dismuke et al.
2014/0367107	A1	12/2014	Hill et al.
2014/0371115	A1	12/2014	Hill et al.
2015/0053404	A1	2/2015	Penny et al.

FOREIGN PATENT DOCUMENTS

CN	103614128		3/2014
CN	103642477		3/2014
EP	1 051 237	B1	11/2003
EP	1 378 554	A1	1/2004
EP	1 786 879	B1	2/2012
EP	2 195 400	B1	8/2012
EP	1 880 081	B1	3/2013
WO	WO 99/49182		9/1999
WO	WO 2005/048706		6/2005
WO	WO 2007/011475		1/2007
WO	WO 2012/158645		11/2012

OTHER PUBLICATIONS

Howard et al., Comparison of flowback aids: understanding their capillary pressure and wetting properties. SPE Production & Operations. Aug. 2010;:376-87.

Kunieda et al. Evaluation of hydrophile-lipophile balance (HLB) of nonionic surfactants. J Colloid and Interface Sci. Sep. 1985;107(1):107-21.

Yang et al., Optimizing nanoemulsions as fluid flowback additives in enhancing tight gas production. J Petroleum Sci Eng. 2014;121:122-5.

Zelenev et al., Microemulsion technology for improved fluid recovery and enhanced core permeability to gas. 2009 SPE European Formation Damage Conference. Scheveningen, The Netherlands. May 27-29, 2009. SPE 122109. 13 pages.

Zelenev et al., Microemulsion-assisted fluid recovery and improved permeability to gas in shale formations. 2010 SPE International Symposium and Exhibition on Formation Damage Control. Lafayette, Louisiana, USA. Feb. 10-12, 2010. SPE 127922. 7 pages.

Zelenev, Surface energy of north American shales and its role in interaction of shale with surfactants and microemulsions. SPE International Symposium on Oilfield Chemistry. The Woodlands, Texas, USA. Apr. 11-13, 2011. SPE-141459. 7 pages.

COMPOSITIONS AND METHODS FOR ENHANCEMENT OF PRODUCTION OF LIQUID AND GASEOUS HYDROCARBONS

RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application Ser. No. 61/644,419 entitled COMPOSITIONS AND METHODS FOR ENHANCEMENT OF PRODUCTION OF LIQUID AND GASEOUS HYDROCARBONS, filed May 8, 2013, the disclosure of which is herein incorporated by reference.

FIELD OF THE INVENTION

The present invention generally relates to the production of petroleum and more particularly to compositions and processes for improving the recovery of liquid and gaseous forms of petroleum from a subterranean geological formation.

BACKGROUND OF THE INVENTION

For many years, petroleum has been recovered from subterranean reservoirs through the use of drilled wells and production equipment. Petroleum hydrocarbons may be produced in a variety of forms, including liquid crude oil, natural gas and light condensates. To enhance the recovery of petroleum, a number of technologies have been developed. Common well stimulation techniques include hydraulic fracturing, water flooding and acidizing operations. Although liquid and gaseous products are typically encountered together, it may be economically desirable to enhance the production of one form of hydrocarbons over another. For example, economic factors may encourage the shift from a predominantly gas-focused production to a production that favors liquid crude oil. Because crude oil and natural gas have very different physical properties, and thus move differently through the porous media of the subterranean formation, the chemicals used for stimulating the well for the purpose of enhancing gas production may not work as effectively in enhancing oil production. As a result, prior art well stimulation and enhancement products have been formulated to recover a particular form of hydrocarbon, i.e., natural gas or liquid crude oil.

To permit the production of multiple forms of hydrocarbons from a given reservoir, well operators are required to use and stock multiple chemicals for treating the same well. Such practice also often requires additional equipment for handling multiple types of chemicals. The use of multiple treatment chemicals increases the cost and complexity of operating the well. Therefore, having a single stimulation product that enhances fluid recovery of multiple forms of hydrocarbons is desirable. It is to these and other objects that the present invention is directed.

SUMMARY OF THE INVENTION

In a preferred embodiment, the present invention includes a well treatment composition that is suitable for the simultaneous enhancement of the production of both liquid and gaseous hydrocarbons from the same reservoir on a non-selective basis. In a specific embodiment, the method provides for increasing the production of oil from a first well having a high gas-to-oil ratio and the production of gas from a second well having a low gas-to-oil ration. The method preferably includes the steps of providing a complex nanofluid additive, emplacing the complex nanofluid additive into the first well and emplacing the same complex nanofluid additive into the second well.

In another aspect, the novel well treatment composition includes a first surfactant and a second surfactant, wherein the second surfactant is selected from the group consisting of ethoxylated alkylene amines, ethoxylated alkyl amines, propoxylated alkylene amines, propoxylated alkyl amines, ethoxylated-propoxylated alkylene amines and ethoxylated-propoxylated alkyl amines. The well treatment composition also includes a first solvent, a second solvent and water. The first solvent is preferably suspended as an internal phase with an external phase created by the water by the first and second surfactants.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In a preferred embodiment, the present invention includes a well treatment composition that is suitable for the simultaneous enhancement of the production of both liquid and gaseous hydrocarbons from the same reservoir on a non-selective basis. In this way, formulations of the preferred embodiments can be used to improve the recovery of liquid and gaseous hydrocarbons during a single treatment operation. The compositions of the preferred embodiments can be used to treat predominantly oil-producing wells to achieve production of gas at commercially viable rates, and to treat predominantly gas-producing wells to achieve production of oil at commercially viable rates.

In preferred embodiments, the complex nanofluid additives of the present invention include: (i) a first surfactant; (ii) a second surfactant, where the second surfactant includes at least one ethoxylated/propoxylated alkylene or alkyl amine surfactant; (iii) one or more solvents with limited solubility in water; (iv) one or more co-solvents; and (v) water. The inventive well treatment additive is characterized as a complex nanofluid that includes at least two normally immiscible solvents stabilized by one or more selected surfactants. In a preferred embodiment, the complex nanofluid includes an internal phase hydrocarbon-based organic solvent distributed in an aqueous external phase.

Preferred conventional surfactants include mixtures of ethoxylated vegetable oils and ethoxylated alcohols. In a more particularly preferred embodiment, the selected surfactant or surfactant mixture has a hydrophile-lipophile balance (HLB) value of between 8 and 18. In a particularly preferred embodiment, the surfactant component is an ethoxylated alcohol. In a more preferred embodiment, the surfactant component is an ethoxylated C8-C18 alcohol. In a still more preferred embodiment, the surfactant component is an ethoxylated C8-C18 alcohol with 5-20 moles of ethylene oxide (EO). In a particularly preferred embodiment, the surfactant component is an ethoxylated vegetable oil. U.S. Pat. No. 7,380,606 issued to Pursley, et. al on Jun. 3, 2008 entitled "Composition and Process for Well Cleaning," which is incorporated herein by reference, discloses several surfactants that function as the surfactant component of the complex nanofluid additive. In certain applications, it may be desirable for the surfactant component to include a mixture of different surfactants and surfactant packages. A particularly preferred surfactant package includes C8-C18 linear alcohol alkoxylates, midrange primary, secondary and tertiary alcohols with between 1 and 10 carbon atoms, C2-C10 glycols, and can also include between 5-30 wt % water. Additionally, the surfactant package can include an ethoxylated vegetable oil.

The second surfactant component is preferably an amine-based surfactant selected from the group consisting of ethoxylated alkylene amines, ethoxylated alkyl amines, propoxylated alkylene amines, propoxylated alkyl amines, ethoxylated-propoxylated alkylene amines and ethoxylated-propoxylated alkyl amines. The ethoxylated/propoxylated alkylene or alkyl amine surfactant component preferably includes more than one nitrogen atom per molecule. Suitable amines include ethylenediaminealcoxylate and diethylenetriaminealcoxylate.

Preferred solvents include organic solvents and more particularly, citrus terpenes. D-limonene provides a suitable and desirable solvent that is normally immiscible in water.

The co-solvent component of the complex nanofluid additive may include a short-chain alcohol having a linear or branched chain with less than about 6 carbon atoms. The co-solvent component may further include glycols and mutual solvents or mixtures of thereof. Unlimited examples of suitable alcohols and glycols include methanol, ethanol, 1-propanol, 2-propanol, isomeric butanols, ethylene glycol, triethlyne glycol, propylene glycol, ethylene glycol monobutyl ether.

Particularly preferred embodiments contain from about 5% to about 40% by weight water, from about 0.05 to about 20% by weight solvent and from about 30% to about 75% by weight of nonionic surfactant mixture, in which a first surfactant is a surfactant with a hydrophile-lipophile balance (HLB) greater than 7, and a second surfactant is an ethoxylated-propoxylated alkylene or alkyl amine with more than one nitrogen atom. In a more particularly preferred embodiment, the amine surfactant component is present in a weight ratio to other surfactants from about 0.01 to about 5 and comprises less than 50% of the total additive formulation.

Additives of the preferred embodiments may also contain from about 10% to about 30% by weight of co-solvents. Additives prepared in accordance with preferred embodiments present a colloidal system with droplets having the mean diameter of less than 200 nm when diluted with an aqueous carrier fluid in a ratio from about 1:10000 to about 1:10. In a particularly preferred embodiment, the solvent to water weight ratio is less than about 2.

The preferred embodiments of the complex nanofluid additives can be prepared by mixing individual components or in-situ by diluting solvent-surfactant blends with a selected carrier fluid, fracturing fluid or acidizing fluid in a batch-tank or on-the-fly during the treatment operation.

The following provides a description of laboratory investigations used to establish the efficacy of the inventive complex nanofluid additives. These experiments included an analysis of the effectiveness of the additives on oil-brine displacement and gas-brine displacement. The complex nanofluid additives of the preferred embodiments were compared against prior-art reference additives.

For the oil-brine displacement experiments, a 25 cm long, 2.5 cm diameter capped glass chromatography column was packed with 77 grams of 100 mesh sand. The column was left open on one end and a PTFE insert containing a recessed bottom, 3.2 mm diameter outlet, and nipple was placed into the other end. Prior to placing the insert into the column, a 3 cm diameter filter paper disc (Whatman, #40) was pressed firmly into the recessed bottom of the insert to prevent leakage of 100 mesh sand. A 2" piece of vinyl tubing was placed onto the nipple of the insert and a clamp was fixed in place on the tubing prior to packing. The columns were gravity-packed by pouring approximately 25 grams of the brine (or brine with chemical treatment) into the column followed by a slow, continuous addition of sand.

After the last portion of sand had been added and was allowed to settle, the excess of brine was removed from the column so that the level of liquid exactly matched the level of the sand. Pore volume in the packed column was calculated as the difference in mass of fluid prior to column packing and after the column had been packed. Three additional pore volumes of brine were passed through the column. After the last pore volume was passed, the level of brine was adjusted exactly to the level of sand bed. Light condensate oil was then added on the top of sand bed to form the 5 cm oil column above the bed. Additional oil was placed into a separatory funnel with a side arm open to an atmosphere.

Once the setup was assembled, the clamp was released from the tubing, and timer was started. Throughout the experiment the level of oil was monitored and kept constant at a 5 cm mark above the bed. Oil was added from the separatory funnel as necessary, to ensure this constant level of head in the column. Portions of effluent coming from the column were collected into plastic beakers over a measured time intervals. The amount of fluid was monitored. When both brine and oil were produced from the column, they were separated with a syringe and weighed separately. The experiment was conducted for 3 hours at which the steady-state conditions were typically reached. The cumulative % or aqueous fluid displaced from the column over 120 minute (2 hour) time period was determined.

For the gas-brine displacement experiments, a 51 cm long, 2.5 cm in diameter capped glass chromatography column was filled with approximately 410±20 g of 20/40 mesh Ottawa sand and a brine (or brine containing chemical treatment). To ensure uniform packing, small amounts of proppant were interchanged with small volumes of liquid. Periodically the mixture in the column was homogenized with the help of an electrical hand massager, in order to remove possible air pockets. Sand and brine were added to completely fill the column to the level of the upper cap. The exact amounts of fluid and sand placed in the column were determined in each experiment. The column was oriented vertically and was connected at the bottom to a nitrogen cylinder via a gas flow controller pre-set at a flow rate of 60 cm^3/min. The valve at the bottom was slowly opened and liquid exiting the column at the top was collected into a tarred jar placed on a balance. Mass of collected fluid was recorded as a function of time by a computer running a data logging software. The experiments were conducted until no more brine could be displaced from the column. The total % of fluid recovered was then calculated.

For these experiments, complex nanofluid additives were prepared in the laboratory by mixing the selected terpene solvent, water, conventional nonionic surfactant with HLB>7, and ethoxylated and propoxylated alkylene or alkyl amine surfactant in ratios described above. All of these constituent components are commercially available from a variety of sources. Typically, the components were mixed together in the order: water, alcohol, nonionic surfactant, ethoxylated-propoxylated alkylene or alkyl amine, and lastly citrus terpene solvent. Other orders of addition are also suitable. The mixtures were then agitated on a magnetic stirrer for 5-10 minutes.

The complex nanofluid additives were then diluted to use concentrations of 1 or 2.0 gallons per 1000 gallons with 2% KCl brine and these diluted fluids were used in gas-oil and gas-brine displacement experiments described above. The selected concentrations are those typically suitable, but other concentrations can be used by those skilled in the art. In addition to the compositions of the present invention, several compositions of the prior art were also prepared. Notably, these prior art reference compositions did not contain the ethoxylated-propoxylated alkylene or alkyl amine component. The reference additives are presented in Table 1 below:

TABLE 1

Reference Additives	
Reference complex nanofluid #1 (NF#1)	
Deionized water:	11.9 wt %
Ethoxylated alcohol nonionic surfactant package	75.1 wt %
co-solvent	8.0 wt %
Citrus terpene:	5.0 wt %
Reference complex nanofluid #2 (NF#2)	
Deionized water:	15 wt %
Ethoxylated alcohol nonionic surfactant package	36.4 wt %
Co-solvent	26.5 wt %
Citrus terpene:	22.1 wt %
Reference complex nanofluid #3 (NF#3)	
Deionized water:	22.5 wt %
co-solvent	35.1%
Pluronic ® surfactant	13.5 wt %
Ethoxylated castor oil:	13.5 wt %
Citrus terpene:	15.4 wt %

The complex nanofluid additives of the preferred embodiments were prepared according to the examples set forth in Table 2:

TABLE 2

Inventive Complex Nanofluid Additives	
Example 1	
Deionized water	16.2 wt %
Ethoxylated alcohol surfactant package	56.1 wt %
2-propanol co-solvent	11.5 wt %
Citrus terpene	4.5 wt %
Ethylenediaminealcoxylate	11.7 wt %
Example 2	
Deionized water	16.2 wt %
Ethoxylated alcohol surfactant package	56.1 wt %
co-solvent	11.5 wt %
Citrus terpene	4.5 wt %
Diethylenetriaminealcoxylate	11.7 wt %
Example 3	
Deionized water	6.4 wt %
Ethoxylated alcohol surfactant package	60.1 wt %
co-solvent	11.5 wt
Citrus terpene	7 wt %
Ethylenediaminealcoxylate	15 wt %
Example 4	
Deionized water	0.4 wt %
Ethoxylated alcohol surfactant package	66.1 wt %
2-propanol co-solvent	11.5 wt %
Citrus terpene	7 wt %
Ethylenediaminealcoxylate	15 wt %

Each of the reference additives and inventive additives were evaluated using the test protocols set forth above. The results of these experiments are summarized in Table 3 below as a percentage of the recovery of brine displacement by gas and brine displacement by oil. Each reference additive and inventive additive was utilized in a concentration range of between 1 gpt and 2 gpt.

TABLE 3

Sample	Effectiveness of brine displacement by gas	Effectiveness of brine displacement by oil
Reference NF#1 1 gpt	80%	38%
Reference NF#2 2 gpt	80%	43%
Reference NF#3 1.5 gpt	25%	80%
Example 1 1 gpt	75%	88%
Example 2 1 gpt	81%	84%
Example 3 1 gpt	59%	88%
Example 4 1 gpt	72%	91%

Based on the results summarized above, it is clear that Reference Additives Nos. 1 and 2 are well-suited for enhancing gas recovery but are not as effective for the recovery of liquid hydrocarbons. Reference Additive No. 3 performed well during the liquid recovery test but did not displace a significant percentage of hydrocarbons during the gas test. Thus, the reference formulations did not demonstrate an ability to effectively recover both liquid and gaseous hydrocarbons. In contrast, the inventive complex nanofluid additives demonstrated effective recovery of both liquid and gaseous hydrocarbons. The ability of these inventive formulations to enhance the recovery of both liquid and gaseous hydrocarbons represents a significant advancement over the prior art.

It is clear that the present invention is well adapted to carry out its objectives and attain the ends and advantages mentioned above as well as those inherent therein. While presently preferred embodiments of the invention have been described in varying detail for purposes of disclosure, it will be understood that numerous changes may be made which will readily suggest themselves to those skilled in the art and which are encompassed within the spirit of the invention disclosed and as defined in the written description. For example, surfactant and surfactant mixture selections can be modified and changed to take into account varying reservoir conditions.

What is claimed is:

1. A method of treating a plurality of hydrocarbon-producing wells, wherein a first of the plurality of hydrocarbon-producing wells has a high gas-to-oil ratio and a second of the hydrocarbon-producing wells has a low gas-to-oil ratio, the method comprising the steps of:

providing a complex nanofluid additive;

emplacing the complex nanofluid additive into the first of the plurality of hydrocarbon-producing wells to lower the gas-to-oil ratio; and

emplacing the complex nanofluid additive into the second of the plurality of hydrocarbon-producing wells to raise the gas-to-oil ratio.

2. The method of claim **1**, wherein before the providing a complex nanofluid additive step, the method further comprises the steps of:

providing a first surfactant and a second surfactant, wherein the second surfactant is selected from the group consisting of ethoxylated alkylene amines, ethoxylated alkyl amines, propoxylated alkylene amines, propoxylated alkyl amines, ethoxylated-propoxylated alkylene amines and ethoxylated-propoxylated alkyl amines;

mixing the first surfactant with the second surfactant to form a surfactant mixture;

adding a first solvent and a second solvent to the surfactant mixture to form a solvent-surfactant mixture;

adding water to the solvent-surfactant mixture to form an emulsified solvent-surfactant mixture; and adding the emulsified-solvent surfactant mixture to a carrier fluid to form the complex nanofluid additive.

3. The method of claim **2**, wherein the second surfactant is ethylenediaminealcoxylate.

4. The method of claim **2**, wherein the second surfactant is diethylenetriaminealcoxylate.

5. The method of claim **2**, wherein the first surfactant includes an ethoxylated alcohol.

6. The method of claim **5**, wherein the first surfactant includes an ethoxylated alcohol having between 8 and 18 carbon atoms and between 5 and 20 moles of ethylene oxide.

7. The method of claim **2**, wherein the second solvent is a co-solvent selected from the group consisting of short-chain alcohols and glycols.

8. The method of claim **2**, wherein the complex nanofluid additive comprises:

up to about 90% by volume of the first surfactant, wherein the first surfactant is selected from the group consisting of nonionic surfactants, cationic surfactants, and anionic surfactants;

up to about 16% by volume of the second surfactant, wherein the second surfactant is selected from the group consisting of ethylenediaminealcoxylate and diethylenetriaminealcoxylate;

up to about 10% by volume of the first solvent, wherein the first solvent is d-limonene; up to about 25% by volume of the second solvent, wherein the second solvent comprises a co-solvent or a mixture of co-solvents; and

up to about 30% by volume water.

9. The method of claim **1**, wherein before the providing a complex nanofluid additive step, the method further comprises the steps of:

providing a first surfactant and a second surfactant, wherein the second surfactant is selected from the group consisting of ethoxylated alkylene amines, ethoxylated alkyl amines, propoxylated alkylene amines, propoxylated alkyl amines, ethoxylated-propoxylated alkylene amines and ethoxylated-propoxylated alkyl amines;

mixing the first surfactant with the second surfactant to form a surfactant mixture;

adding a first solvent and a second solvent to the surfactant mixture to form a solvent-surfactant mixture; and

adding water to the solvent-surfactant mixture to form an emulsified solvent-surfactant mixture, wherein the emulsified solvent-surfactant mixture comprises a concentrated form of the complex nanofluid additive.

10. A method for increasing production of oil from a first well having a high gas-to-oil ratio and production of gas from a second well having a low gas-to-oil ratio, the method comprising the steps of:

providing a complex nanofluid additive;

emplacing the complex nanofluid additive into the first well; and

emplacing the complex nanofluid additive into the second well.

11. The method of claim **10**, wherein before the providing a complex nanofluid additive step, the method further comprises the steps of:

providing a first surfactant and a second surfactant, wherein the second surfactant is selected from the group consisting of ethoxylated alkylene amines, ethoxylated alkyl amines, propoxylated alkylene amines, propoxylated alkyl amines, ethoxylated-propoxylated alkylene amines and ethoxylated-propoxylated alkyl amines;

mixing the first surfactant with the second surfactant to form a surfactant mixture;

adding a first solvent and a second solvent to the surfactant mixture to form a solvent-surfactant mixture;

adding water to the solvent-surfactant mixture to form an emulsified solvent-surfactant mixture; and

adding the emulsified-solvent surfactant mixture to a carrier fluid to form the complex nanofluid additive.

12. The method of claim **11**, wherein the second surfactant is ethylenediaminealcoxylate.

13. The method of claim **11**, wherein the second surfactant is diethylenetriaminealcoxylate.

14. The method of claim **11**, wherein the first surfactant includes an ethoxylated alcohol.

15. The method of claim **11**, wherein the first surfactant includes an ethoxylated alcohol having between 8 and 18 carbon atoms and between 5 and 20 moles of ethylene oxide.

16. The method of claim **11**, wherein the second solvent is a co-solvent selected from the group consisting of short-chain alcohols and glycols.

17. The method of claim **11**, wherein the complex nanofluid additive comprises:

up to about 90% by volume of the first surfactant, wherein the first surfactant is selected from the group consisting of nonionic surfactants, cationic surfactants, and anionic surfactants;

up to about 16% by volume of the second surfactant, wherein the second surfactant is selected from the group consisting of ethylenediaminealcoxylate and diethylenetriaminealcoxylate;

up to about 10% by volume of the first solvent, wherein the first solvent is d-limonene; up to about 25% by volume of the second solvent, wherein the second solvent comprises a co-solvent or a mixture of co-solvents; and

up to about 30% by volume water.

18. The method of claim **10**, wherein before the providing a complex nanofluid additive step, the method further comprises the steps of:

providing a first surfactant and a second surfactant, wherein the second surfactant is selected from the group consisting of ethoxylated alkylene amines, ethoxylated alkyl amines, propoxylated alkylene amines, propoxylated alkyl amines, ethoxylated-propoxylated alkylene amines and ethoxylated-propoxylated alkyl amines;

mixing the first surfactant with the second surfactant to form a surfactant mixture;

adding a first solvent and a second solvent to the surfactant mixture to form a solvent-surfactant mixture; and

adding water to the solvent-surfactant mixture to form an emulsified solvent-surfactant mixture, wherein the emulsified solvent-surfactant mixture comprises a concentrated form of the complex nanofluid additive.

* * * * *